JRC Scientific and Technical Reports

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EUR 22115 EN - 2007

JRC EUROPEAN COMMISSION

Institute for Reference Materials and Measurements

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Joint Research Centre
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http://www.jrc.ec.europa.eu

EUR 22115 EN
ISBN 92-79-01631-8
ISSN 1018-5593

Luxembourg: Office for Official Publications of the European Communities

Printed in Belgium

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Summary

This certification report describes the processing and characterisation of IRMM-521R, a certified reference material (CRM) consisting of nickel metal foil for neutron dosimetry applications. To avoid spectral interference due to cobalt impurities, IRMM-521R has a certified upper limit of cobalt content, thus reducing the uncertainty of dosimetry measurements. IRMM-521R consists of a high purity nickel foil with a cobalt content of < 0.26 mg/kg. With a 95 % probability, the cobalt content of samples of IRMM-521R is below this level.

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Glossary

ASTM	American Society for Testing and Materials
CRM	Certified Reference Material
DC	Direct Current
EC	European Commission
ICP-SF-MS	Inductively Coupled Plasma Sector Field Mass Spectrometry
INAA	Instrumental Neutron Activation Analysis
IRMM	Institute for Reference Materials and Measurements, Directorate General Joint Research Centre, European Commission
k	Coverage factor
k_0-NAA	Neutron Activation Analysis using the k_0-method for quantification
NAA	Neutron Activation Analysis
p	Number of laboratories involved in the certification
NRM	Nuclear Reference Material
RSD	Relative Standard Deviation
s	Standard deviation
$s_{between\text{-}b}$	Variation of results obtained on different buttons
$s_{between\text{-}l}$	Variation of results obtained at different laboratories
s_{bb}	Between-unit standard deviation
SI	Système International d'unités (international system of units)
SSMS	Spark Source Mass Spectrometry
$s_{within\text{-}b}$	Within-button standard deviation
$s_{within\text{-}l}$	Within-laboratory standard deviation
t	Student's t-factor
u_{bb}	Standard uncertainty related to between-button inhomogeneity
u_c	Combined uncertainty of the certified value
u_{char}	Standard uncertainty of the characterisation
u_{lts}	Standard uncertainty of the long-term stability
$\bar{x}$	Mean of laboratory mean values

1. Introduction

1.1. Reactor neutron dosimetry

Reactor neutron dosimeters are used for the safety surveillance of nuclear reactor vessels. Steel test specimens are irradiated in the reactor together with dosimetry materials in order to detect and measure small property changes of the vessel steel during reactor operation. From the results of these surveillance measurements, the assessment of the duration of safe operation of the reactor, and hence of its operational lifetime, is made. The quality of measurement results and their comparability with those obtained elsewhere is strongly dependent from the quality of the dosimeter material and its characterisation and requires thorough standardisation.

1.2. Significance of cobalt content of nickel-based dosimeter materials

High purity nickel metal is used in neutron metrology to monitor fast neutron fluence rates and fluences. For example, ASTM E 264 [1] describes the procedure for determining neutron flux density by the activation reaction ^{58}Ni(n,p) ^{58}Co. The nuclide of interest is ^{58}Ni. A problem arises due to possible spectral interference of ^{59}Co(n,γ) caused by thermal neutrons (Table 1). Therefore nickel metal with low cobalt content is required as a reference material to be used for reactor surveillance, interlaboratory comparisons and other neutron metrology requirements. This is the rationale for producing the CRM IRMM-521R with certified, low cobalt content.

1.3. Certification of EC-NRM 521

In 1988, a nickel metal for reactor neutron dosimetry was certified as EC-NRM 521 [2]. EC-NRM 521 consists of nickel with a nominal purity of 99.99 %, the isotopic abundances corresponding to the natural composition. The level of cobalt present as impurity and causing mainly spectral interference during application is certified, and the certified upper cobalt mass fraction is 0.1 mg/kg. Since cobalt levels of 1 mg/kg can lead to a contribution of 3 % to the dosimeter uncertainty, a content of 0.25 mg/kg can be considered sufficiently low (uncertainty contribution < 0.8 %) to neglect the influence of secondary nuclear reactions when irradiating the nickel foil for neutron metrology.

EC-NRM 521 was available in two physical shapes: 100 cm^2 units of 0.1 mm thick foil (EC-NRM 521A) and of 1 m units of 0.5 mm diameter wire (EC-NRM 521B). The certified cobalt mass fraction was based on 38 accepted results carried out by five laboratories using three different methods: neutron activation analysis (NAA), inductively coupled plasma optical emission spectroscopy and atomic absorption spectrometry. NAA and spark source mass spectrometry were used to verify the overall purity, whereas thermal ionisation mass spectrometry was used to verify the isotopic composition.

1.4. Certification of IRMM-521R

The foil material, EC-NRM 521A is now sold out. It was therefore decided to certify a new batch of nickel metal foil of 0.1 mm thickness to replace EC-NRM

521. A full certification study was performed to determine the cobalt content of the nickel foil, the intention being to certify an upper limit of Cobalt mass fraction.

Table 1: Reactions and transitions of interest for reactor neutron dosimetry using pure nickel metal [3].

Reactions and transitions of interest:	
$^{58}Ni(n,p)\ ^{58m}Co$	$\langle\sigma\rangle = 3.40\,10^{-26}$ cm^2
$^{58}Ni(n,p)\ ^{58}Co$	$\langle\sigma\rangle = 7.45\,10^{-26}$ cm^2
$^{58}Co^{m} \xrightarrow{IT} {}^{58}Co$	$t_{1/2} = 9.15$ h
$^{58}Co^{m}(n,\gamma)^{59}Co$ (a)	$\sigma = 1.36\,10^{-19}$ cm^2
$^{58}Co\ (n,\gamma)^{59}Co$ (a)	$\sigma = 1.88\,10^{-21}$ cm^2
$^{58}Co \xrightarrow{\beta^+} {}^{58}Fe$ (a)	$t_{1/2} = 70.80$ d
Nuclear interference:	
$^{59}Co(n,2n)^{58}Co$	$\langle\sigma\rangle = 4.0\,10^{-28}$ cm^2
Spectral interferences:	
$^{59}Co(n,\gamma)^{60m}Co$	$\sigma = 2.0\,10^{-23}$ cm^2
$^{60}Ni(n,p)^{60m}Co$	$\langle\sigma\rangle = 2.1\,10^{-27}$ cm^2
$^{59}Co(n,\gamma)^{60}Co$	$\sigma = 1.7\,10^{-23}$ cm^2
$^{60}Ni(n,p)^{60}Co$	$\langle\sigma\rangle = 2.3\,10^{-27}$ cm^2
$^{60}Co^{m} \xrightarrow{IT} {}^{60}Co$	$t_{1/2} = 10.47$ min
$^{60}Co \xrightarrow{\beta^-} {}^{60}Ni$ (a)	$t_{1/2} = 5.271$ y
(a) : stable nuclides; $t_{1/2}$: half-life; σ : cross section; $\langle\sigma\rangle$: cross section averaged over a fission spectrum	

2. Participants

Processing of the nickel material was performed at the Reference Materials Unit of the Institute for Reference Materials and Measurements, Joint Research Centre, European Commission, in Geel, Belgium.

The following laboratories contributed to the certification of IRMM-521R:

- Central Science Laboratory, Sand Hutton (UK)
- Centre National de la Recherche Scientifique, Service Central d'Analyse, Vernaison (FR)
- Nuclear Research and consultancy Group, Petten (NL)
- Bundesanstalt für Materialforschung und –prüfung, Berlin (DE)
- Isotope Measurements Unit, Institute for Reference Materials and Measurements, Joint Research Centre, European Commission, Geel (BE)
- Department of Chemistry, Universiteit Antwerpen (BE)

3. Processing

IRMM-521R was prepared using nickel oxide of nominal purity 99.995 % (Alfa, Johnson Matthey Company, Karlsruhe, batch no. 22356; 3.4 kg). The certificate of analysis indicates that no cobalt was detected by DC arc emission spectroscopy (detection limit for Co 1 mg/kg). Only Ca (2 mg/kg) and Cu (2 mg/kg) were detected as impurities.

The nickel oxide was reduced in a tube furnace. The powder was placed in a quartz boat, and heated to 700 °C for 60 minutes under a flow of hydrogen gas. The resulting metal powder was then melted by cold crucible melting [4] into 13 buttons of about 300 g, of which 12 buttons were successfully rolled [5] to a thickness of nominally 0.1 mm on a cold rolling mill (Basildon, Albert Mann). (Button 13 cracked during initial rolling steps, prohibiting further rolling to the required thickness). The size of the resulting foils was at least 5 x 15 cm².

The foil samples were cleaned with alcohol, wrapped in tissues and packed in plastic envelopes at IRMM, where they are stored at room temperature. Samples are cut to the desired size with scissors from the rolled foils as orders are received.

4. Stability

The stability of the cobalt content in nickel is guaranteed by the high degree of solubility of Co atoms in the α-phase of nickel (αCo,Ni) [6]. Actually, in industrial practice, nickel-based alloys are used in which cobalt is added to render nickel more heat and chemical resistant. It is therefore not likely that the cobalt content of IRMM-521R will change during storage at room temperature or transport at temperatures assumed to be below 60 °C.

5. Isotopic abundance

The isotopic abundance of Ni has been verified at the Isotope Measurements Unit of IRMM [7]. Samples were wiped with ethanol, weighed, placed in fluoroethylene-polypropylene bottles and dissolved in 6 % HNO_3. Two measurement methods (method 1 and method 2) were developed to determine major and minor isotope ratios - ^{58}Ni, ^{60}Ni, ^{62}Ni in method 1 and ^{61}Ni, ^{62}Ni, ^{64}Ni in method 2. For each measurement method, 6 samples were prepared (2 replicates of three buttons). By two-step dilution, solutions with ~40 and 400 mg Ni kg^{-1} were prepared for method 1 and method 2 respectively. The mass spectrometry measurements were performed on a sector field high resolution ICP-MS Thermo Finnigan Element2. The correction for mass discrimination was performed specifically for each pair of isotopes using the bracketing approach with mono-elemental Ni standard solution with natural isotopic composition Johnson Matthey (Ni content of ~ 40 and 400 µg Ni kg^{-1} for method 1 and method 2, respectively). After each sample (or sample for mass discrimination correction) a sufficient time was allowed (~7 min) to avoid memory effects. Additionally, a blank data acquisition was made at the end of each rinse period. Table 2 shows that, within their uncertainty (relative uncertainty values between 0.25 and 0.6 %), the measured data agree with the data of representative isotopic compositions [8].

Table 2: Ni isotopic composition in IRMM-521R.

	Measured data		Reference data from [8]	
	Amount fraction (%)	Uncertainty (k = 2, 95 % confidence level) (%)	Amount fraction (%)	Uncertainty (k = 2, 95 % confidence level) (%)
$n(^{58}Ni)/n(Ni)$	68.12	0.17	68.0769	0.0089
$n(^{60}Ni)/n(Ni)$	26.20	0.16	26.2231	0.0077
$n(^{61}Ni)/n(Ni)$	1.136	0.006	1.1399	0.0006
$n(^{62}Ni)/n(Ni)$	3.626	0.016	3.6345	0.0017
$n(^{64}Ni)/n(Ni)$	0.9220	0.0048	0.9256	0.0009

6. Overall purity assessment

An assessment of the overall purity of the nickel reference material was made to confirm the absence of impurities, which disturb neutron induced gamma-spectra.

6.1. Method used: spark source mass spectrometry

The technique used to detect the broad range of possible impurities was spark source mass spectrometry (SSMS). The SSMS results have a reproducibility of 30 %, which is sufficient to estimate the level of impurities in the nickel reference material. SSMS is based on the formation of ions from a solid sample in a radiofrequency spark under vacuum. The produced positive ions are accelerated and after energy selection, separated according to mass to charge ratio in a magnetic field. The detection of the ions happens simultaneously on an ion sensitive emulsion (photographic plate). A JEOL JMS-01-BM2 double focussing spark source mass spectrometer was used, and a NEYCO digital micro densitometer, to which a micro-photometer of ZEISS type SI n° 313340 is connected (for reading the photographic plates).

6.2. Samples and reference materials

Samples of Ni IRMM-521 AR (foil 0.1 mm thickness) and Ni IRMM-521 B (wire 0.5 mm diameter) were tested. Samples were folded to obtain a sample thickness acceptable for having stable measurements. For the sample IRMM-521R 3 analyses were made, for the sample IRMM-521B, which serves as a quality control material, 1 analysis was made. During 20 minutes the samples were presparked (without detection on the photoplate) to clean for eventual surface impurities. A Ni standard produced by Goodfellow for which the content of a number of elements are known is used. The signal from the 'standard' is collected on the same photoplate as the unknown sample. By comparing the intensities of the elements present in the unknown as well as in the 'standard' sample intensities were converted to concentrations.

6.3. Results

The results obtained on the IRMM-521B sample agree with the purity results reported in the corresponding certification report [2]. This indicates that the results obtained are reliable. The results of the three replicate analyses of the IRMM-521R sample are shown in Table 3. This table shows only the results for the elements, which were detected at levels above the detection limit. For other elements the detection limit was not reached. These elements and the corresponding detection limits are shown below Table 3.

Table 3: Results of SSMS to assess the purity of IRMM-521R.

	replicates			combined results 1-3		
element	1	2	3	mean	s	RSD
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%
Li	0.015	0.010	0.013	0.013	0.003	20
B	0.011	0.012	0.010	0.011	0.001	9
C	20	19	28	22	5	22
N	2.5	0.7	2.5	1.9	1.0	55
O	520	640	450	537	96	18
Na	18	25	16	20	5	24
Mg	1.2	1.3	1.2	1.2	0.1	5
Al	2.3	1.5	1.5	1.8	0.5	26
Si	3.9	5.3	5.2	4.8	0.8	16
S	3.1	2.3	4.5	3.3	1.1	34
Cl	2.3	1.5	3.3	2.4	0.9	38
K	1.0	1.3	1.2	1.2	0.2	13
Ca	2.5	2.2	1.7	2.1	0.4	19
Ti	0.22	0.15	0.25	0.21	0.05	25
Cr	1.10	0.74	0.66	0.83	0.23	28
Mn	0.23	0.21	0.16	0.20	0.04	18
Fe	33	26	23	27	5	19
Co	0.22	0.22	0.29	0.24	0.04	17
Cu	1.5	1.2	1.4	1.4	0.2	11
Zn	0.17	0.17	0.11	0.15	0.03	23
Ge	0.50	0.25	0.23	0.33	0.15	46
As	5.2	6.8	6.6	6.2	0.9	14
Br	0.6	0.7	0.9	0.7	0.2	21
Te	14	12	16	14	2	14
Pb	0.9	0.9	1.3	1.0	0.2	21
Bi	0.49	0.49	0.66	0.55	0.10	18

Elements not detected and their detection limit: Be (< 0.001), F (< 0.005)*, Sc (< 0.03), V (< 0.02), Ga (< 0.03), Se (< 0.1)*, Rb (< 0.03), Sr (< 0.03), Y (< 0.02), Zr (< 0.15), Nb (< 0.025), Mo (< 0.1), Ru (< 0.09), Rh (< 0.03), Pd (< 0.1), Ag (< 2), Cd (< 0.1), In (< 0.04), Sn (< 0.15), Sb (< 0.07), I (< 0.04)*, Cs (< 0.04), Ba (< 0.06), La (< 0.05), Ce (< 0.05), Pr (< 0.05), Nd (< 0.2), Sm (< 0.2), Eu (< 0.1), Gd (< 0.2), Tb (< 0.06), Dy (< 0.2), Ho (< 0.06), Er (< 0.2), Tm (< 0.06), Yb (< 0.2), Lu (< 0.07), Hf (< 0.25), Ta (< 1), W (< 0.2), Re (< 0.1), Os (< 0.2), Ir (< 0.2), Pt (< 0.2), Au (< 0.5), Hg (< 0.6), Tl (< 0.1), Th (< 0.1), U (< 0.1).

Elements indicated with a * (F, Se, I) can evaporate before ionisation takes place. The obtained value is possibly too low. Also, it must be noted that the element P is interfered by $^{62}Ni^{++}$.

6.4. Conclusion

Summing all measured impurity contents, a total of about 650 mg/kg is obtained. It is noted, however, that the oxygen content is rather high (0.5 g/kg). This is due to the fact that IRMM-521R was prepared starting from a pure nickel oxide powder. Since oxygen does not disturb neutron induced gamma-spectra, this does not affect the suitability of the IRMM-521R material for the intended use.

7. Characterisation of Co content

7.1. Methods used

The characterisation of the cobalt mass fractions was performed in 4 laboratories, each of which received 8 samples taken from 4 different foils (see also Figure 4). The methods selected had to provide results which are traceable to the SI. The methods used in the characterisation study are NAA and Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SF-MS). Details of the procedures followed, are summarised in Annex 1. Individual results of the participants are displayed in Annex 2.

7.2. Evaluation of results

To detect outliers and the normality of the data distribution more easily, Figure 1 shows the individual measurements ranked according to their value, pooled for all laboratories. The graph shows that data are evenly distributed all across the range of values measured (between 0.15 mg/kg and 0.27 mg/kg), and there is no indication that the values at the extremes are statistical outliers.

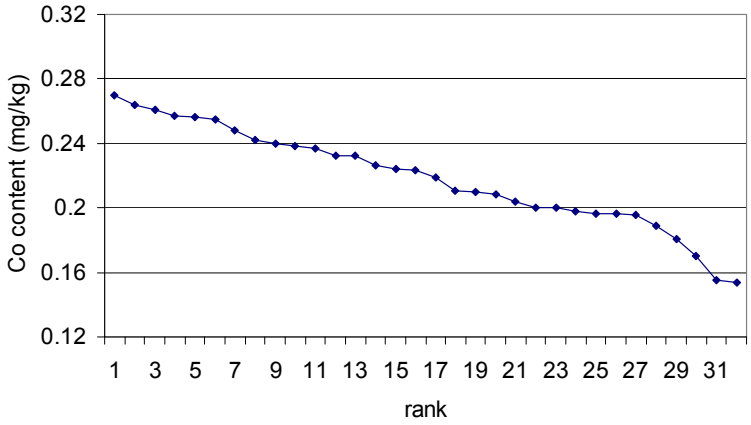

Figure 1: Overview of all measurements, ranked according to the measured value.

The even distribution of all measured values (Figure 1) indicates that the distribution is not Gaussian. The reason for the non-Gaussian distribution is probably the systematic differences between laboratories, as indicated in Figure 2, which shows the measurements grouped per lab. This figure also indicates that there is no grouping according to method (NAA vs. HR-ICP-MS).

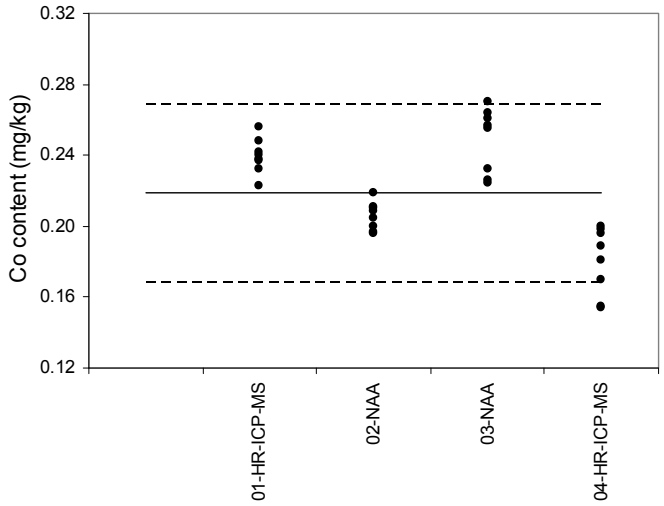

Figure 2: Distribution of individual measurement results for each lab. Given the limited number of participating laboratories, the 95 % confidence interval, indicated is obtained by multiplying the between-laboratory standard deviation with a t-factor of 3.18.

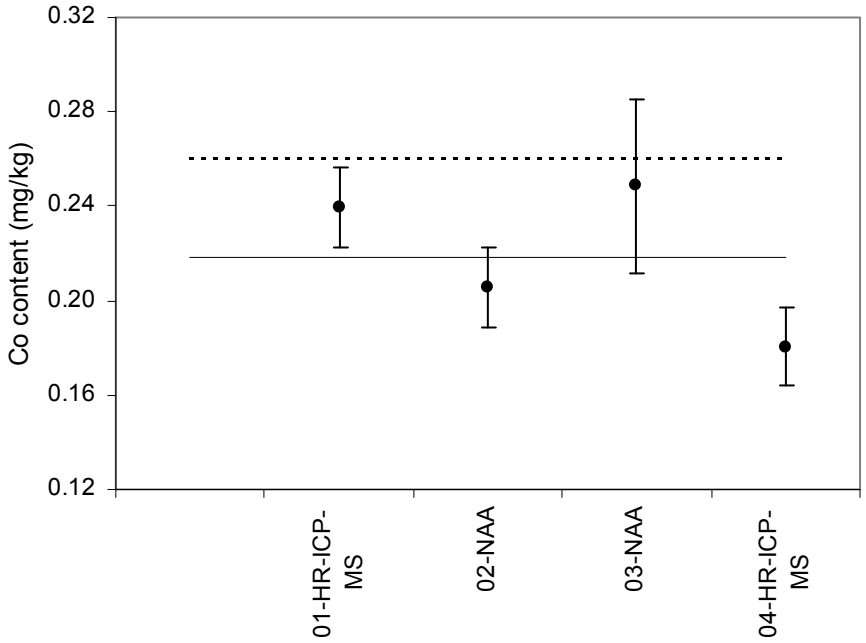

Figure 3: Laboratory averages with expanded uncertainties (k = 2, 95 % confidence level) as reported by the laboratories. The solid line indicates the mean of laboratory means. The dashed line indicates the certified upper limit value of the cobalt content (at a confidence level of about 95 %).

The mean of laboratory means, and its uncertainty, estimated as $u_{char} = \frac{s}{\sqrt{p}}$, with *s* the standard deviation of the laboratory mean values and *p* the number of participating laboratories, are shown in Table 4.

Table 4: Result of the characterisation tests.

Analyte	**Number of valid datasets**	**Mean of laboratory means** [mg/kg]	u_{char} [mg/kg]	u_{char} [%]
Co	4	0.219	0.016	7.2

8. Homogeneity and minimum sample intake

8.1. Between-sample homogeneity

Homogeneity of IRMM-521R was assessed using the data obtained in the characterisation study on samples taken from uniquely coded foils distributed over the whole batch (12 buttons). 32 samples were taken from all of the 12 buttons, with a minimum of 2 samples per button. First, the possible presence of a trend throughout the buttons was investigated. Figure 4 reveals such trend, but this trend is shown to be insignificant (t-test, confidence level 95%).

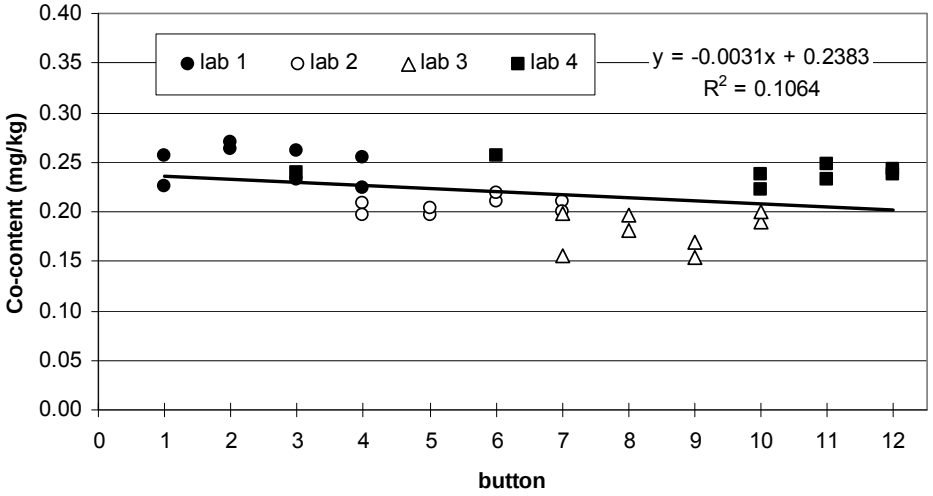

Figure 4: Results of tests on 32 samples taken from foils from all 12 nickel buttons. The regression line is indicated.

Figure 4 indicates clearly, but qualitatively, that the major difference between the results stems from the laboratory where the test was performed, and not from the button from which the sample was taken. To make more quantitative statements about this observation, two one-way ANOVA analyses were carried out.

Table 5: ANOVA of the characterisation data grouped per button.

Button	*Count*	*Sum*	*Average*	*Variance*
1	2	0.483	0.2415	0.000481
2	2	0.534	0.267	1.8E-05
3	2	0.493	0.2465	0.000421
4	2	0.479	0.2395	0.000481
5	2	0.4004	0.2002	3.2E-05
6	2	0.4286	0.2143	3.87E-05
7	2	0.4105	0.20525	5.94E-05
8	2	0.377	0.1885	0.000113
9	2	0.324	0.162	0.000128
10	2	0.389	0.1945	6.05E-05
11	2	0.48	0.24	0.000128
12	2	0.48	0.24	8E-06

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.020405	11	0.001855	11.31866	0.000103	2.717329
Within Groups	0.001967	12	0.000164			
Total	0.022371	23				

The first analysis (Table 5) investigates the data grouped by button. The dispersion between buttons ($s_{between-b} = \sqrt{\frac{(MS_{between-b} - MS_{within-b}}{n}}$, with n = 2 = number of data/button), is 0.029 mg/kg.

Table 6: ANOVA of the characterisation data grouped per laboratory.

Labs	*Count*	*Sum*	*Average*	*Variance*
1	8	1.989	0.248625	0.000336
2	8	1.6443	0.205538	6.11E-05
3	8	1.443	0.180375	0.000352
4	8	1.916	0.2395	9.83E-05

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between-labs	0.02376	3	0.00792	37.39986	6.28E-10	2.946685
Within-labs	0.00593	28	0.000212			
Total	0.02969	31				

In the second ANOVA analysis (Table 6), data were grouped by laboratory. The dispersion between laboratories ($s_{between-l} = \sqrt{\frac{(MS_{between-l} - MS_{within-l}}{n}}$, with n = 8 = number of data/laboratory), is larger than the dispersion between data from the same button.

The comparison of the two ANOVA analyses indicates that the larger part of the dispersion stems from the between-laboratory deviation. In this case, the within-laboratory dispersion ($s_{within-b} = \sqrt{MS_{within-b}}$) is a more realistic, but still a

conservative estimate for the material heterogeneity than the between-button dispersion. The value of $s_{within\text{-}l}$ (0.015 mg/kg) will therefore be used further as u_{bb}.

8.2. Minimum sample intake

The intended use of IRMM-521R does not require a small sample intake. Relatively large parts of the 0.1 mm thick foil are used as dosimetry material. Therefore, no particular microhomogeneity study was performed. Since all laboratories used similar sample intakes of about 150 mg, by definition this amount is sufficient to achieve the repeatability in the characterisation exercise. A mass of 150 mg corresponds with a foil of 2 cm².

9. Certified value and associated uncertainty

9.1. Certified values and uncertainties

The certified maximum cobalt content is obtained as the sum of the mean of the means of the laboratories (0.219 mg/kg), and a value which reflects the uncertainty of obtaining this value on any given sample. This uncertainty is calculated according to following equation, using relative uncertainties.

$$u_c = \sqrt{u_{bb}^2 + u_{lts}^2 + u_{char}^2}$$

Combining the contributions u_{char} and u_{bb} (the contribution from long-term stability, u_{lts}, is negligible), the value of u_c is 0.022 mg/kg.

To obtain the certified upper value of the cobalt content in IRMM-521R, at a stated level of confidence of 95 %, one adds the laboratory mean value, which is the best estimate of the mean cobalt mass fraction, and a suitably expanded u_c. The degrees of freedom corresponding with u_{char} and u_{bb} are 3 and 28, respectively. Using the Welch-Sattertwaithe equation, one obtains that the degrees of freedom of u_c equals 9. Therefore, to obtain a 95 % confidence for the upper limit of cobalt content, one can multiply the value of u_c with t(0.1, 9) = 1.83, the t-factor for a one-sided 95 % confidence interval:

$$CV = \bar{x} + t(0.1,\ 9) \cdot u_c$$

The certified value for IRMM-521R is shown in Table 7.

Table 7: Certified upper limit to the cobalt mass fraction in IRMM-521R at a 95 % confidence level.

	Mass fraction [mg/kg]
Cobalt	< 0.26

9.2. Traceability

Traceability of the certified value to the SI is ensured through the set-up of the characterisation. The participating laboratories used a number of fully independent methods for the sample preparation as well as for the final determination, thus eliminating any possibility of method dependent results. In addition, different calibrants have been used, including commercial standard solutions, CRMs and in-house gravimetrically prepared calibrants.

9.3. Commutability

The intended use of IRMM-521R is related directly to the cobalt mass fraction, which is the certified property. Therefore, commutability is assured.

10. Intended use and instructions for use

This CRM is intended to be used in neutron metrology to monitor fast neutron fluence rates and fluences. The nuclide of interest is ^{58}Ni.

Samples can be stored at 18 °C.

The reduction of the size of the sample to suit the lateral dimensions of a particular type of instrument is allowed. A minimum sample intake of 150 mg (corresponding with a foil of 2 cm²) is recommended.

Before use it is recommended to clean the sample in an ultrasonic bath for 5 minutes in ethanol, to rinse it with distilled water also using an ultrasonic bath for 5 minutes, and to dry it in a dust-free environment at room temperature.

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Acknowledgements

The authors would like to thank S. Trapmann, H. Emteborg, J. Pauwels, T. Linsinger, and H. Emons (IRMM) for the reviewing of the certification report, as well as the experts of the Certification Advisory Panel 'Elements and inorganic ions', O. Donard (Université de Pau et des pays de l'Adour, FR), L. Jorhem (National Food Administration, SE) and H. Muntau (Ranco, IT) for their comments.

Annex 1: Summary of methods used for characterisation.

The combination of lab code and method acronym allows identification of the results in the graphs and tables of Annex 2.

Lab code	Method acronym	Nominal Sample mass (mg)	Sample preparation	Calibrants	Instrumentation and measurement method
01	ICP-SF-MS	200	Test solutions prepared from full discs, using dilute nitric acid (20 mL of 15 %), agitated overnight, aliquot of each test solution (1 mL) diluted to a final volume of 5 mL prior to measurement.	Range of acid matched standards (between 0 and 8 µg/l Co) using commercial Co, Ni, Ga standards "traceable" to NIST-CRMs (Aristar); ^{70}Ga as an internal standard; SRM 1640 (trace elements in natural water, Co: 20.38 µg/L) for analyte recovery estimation.	ThermoFinnigan 'Axiom' high resolution inductively coupled plasma - mass spectrometer (ICP-SF-MS); optimised for maximum sensitivity on ^{115}In; resolution pushed to separate polyatomic interference between ^{58}Ni+^{1}H and ^{59}Co.

Lab code	Method acronym	Nominal Sample mass (mg)	Sample preparation	Calibrants	Instrumentation and measurement method
02	NAA	200	Full samples digested in 30 % HCl (Merck, UltraPure) and 1 mL 65 % HNO_3 (Merck UltraPure) and heated to 100 °C, until near dryness (repeated once); residue dissolved in 30 % HCl (Merck, UltraPure), evaporated to dryness at 150 °C; residue dissolved in 30 % HCl (Merck, UltraPure); separation of Co: Bio-Rad AG 1X8 anion-exchange colums, equilibrated with 15 % HCl and 30 % HCl (Merck, UltraPure). Effluent fraction contains 99.8 % of the Ni burden of the column, Co eluted with 15 % HCl (Ultra-Pure); effluent collected in Teflon beakers, which are heated until 5 mL remains.	Two standards and two blanks also processed in the analytical procedure. Standards are 2 aliquots of NIST SRM 3172a (Multi-element Mix B-1 standard solution, Co = 110.3 mg/kg), pipetted into the PE bags.	Samples, blanks and standards irradiated simultaneously for 8 hours in a thermal neutron flux of 3 x 10^{11} $cm^{-2}.s^{-1}$, 2 weeks decay time, counted for 24 hours in a low background 300 cm^3 well-type Ge detector, Spectral deconvolution is done by Canberras Genie2K.

Lab code	Method acronym	Nominal Sample mass (mg)	Sample preparation	Calibrants	Instrumentation and measurement method
03	NAA	140	No sample pre-treatment (no digestion, no preconcentration or separation steps).	Solution prepared from electrolytic cobalt metal (99.9 %), concentration 1.0086 mg/g (main impurities S, C, Fe, Ni = 0.065 %, Mn) in 10 mL HNO_3 (65 % Suprapur), 8 mL HF (40 % pro analyse) and 16 mL H_2O_2 (30 % Suprapur), diluted with deionised water to 1.0086 mg/g.	Irradiation time approx; 30 days, cold neutron flux approx. 9×10^8 $cm^{-2}.s^{-1}$; cooling time approx. 30 days; samples and calibration substances measured sequentially with high purity Ge-detector, 1173 keV and 1333 keV γ-lines of ^{60}Co used.
04	ICP-SF-MS	140	Mineralisation of sample in a PTFE beaker with 10 mL nitric acid (Merck Suprapur), heat to 100 °C during 15 to 20 minutes until the sample is dissolved, dilution with 200 mL demineralised H_2O.	Calibration solutions prepared at 0, 0.25, 0.5, 1.0 and 2.0 µg/L prepared in same matrix (5 % HNO_3) from certified solution (SPEX) at 1 g Co/L (matrix: cobalt nitrate in 2 % HNO_3); internal standard ^{115}In isotope (10 µg/L)	ICP-SF-MS (Element Thermoquest Finnigan); ^{59}Co; Internal standard : ^{115}In

Annex 2: Data from characterisation study

(All data in mg/kg.)

Lab	Method	n	mean	*s*	RSD	95%CI	Individual results							
01	HR-ICP-MS	8	0.2395	0.0099	4.1%	0.0083	0.237	0.223	0.248	0.232	0.238	0.242	0.240	0.256
02	NAA	8	0.2055	0.0078	3.8%	0.0065	0.208	0.197	0.196	0.204	0.210	0.219	0.211	0.200
03	NAA	8	0.2486	0.0183	7.4%	0.0153	0.226	0.257	0.264	0.270	0.232	0.261	0.224	0.255
04	HR-ICP-MS	8	0.1804	0.0188	10.4%	0.0157	0.198	0.155	0.196	0.181	0.154	0.170	0.189	0.200

European Commission

EUR 22115 EN – Joint Research Centre – Institute for Reference Materials and Measurements
Title: Certification of cobalt in a nickel metal reference material for neutron dosimetry, IRMM-521R
Author(s): G. Roebben, K. Teipel, C. Ingelbrecht, A. Lamberty
Luxembourg: Office for Official Publications of the European Communities
2007 – 24 pp. – 21.0 x 29.7 cm
EUR – Scientific and Technical Research series – ISSN 1018-5593
ISBN 92-79-01631-8

Abstract

This certification report describes the processing and characterisation of IRMM-521R, a certified reference material (CRM) consisting of nickel metal foil for neutron dosimetry applications. To avoid spectral interference due to cobalt impurities, IRMM-521R has a certified upper limit of cobalt content, thus reducing the uncertainty of dosimetry measurements. IRMM-521R consists of a high purity nickel foil with a cobalt content of < 0.26 mg/kg. With a 95 % probability, the cobalt content of samples of IRMM-521R is below this level.

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ISBN 92-79-01631-8
9 789279 016318